

p Si, due to electrostatic repulsion effects between the positively charged copper precipitates and interstitial copper ions. Comparison of the impact of Cu on minority carrier diffusion length obtained with *p*-Si samples of different resistivity confirmed the electrostatic model. Studies of the impact of copper on minority carrier diffusion length in samples with internal gettering sites indicated that they provide heterogeneous nucleation sites for Cu precipitation at subcritical Cu concentration. Above a certain threshold of Cu concentration, the bulk recombination activity is dominated by quasihomogeneous formation of Cu precipitates, a process that is not detectably affected by the presence of oxide precipitates. © 2001 American Institute of Physics. [DOI: 10.1063/1.1415350]

Copper is one of the most common metal contaminants in silicon. The detrimental impact of copper on semiconductor device yield was recognized already in 1960 by Goetzberger and Shockley.¹ However, systematic studies of the properties of copper in silicon were complicated by the lack of measurement techniques to reliably detect copper in trace concentration in silicon. Therefore, until recently, Cu in Si was much less understood than, e.g., Fe in Si. In particular, literature data on the impact of copper on minority carrier diffusion length were controversial. It was found^{2–8} that intentional Cu contamination up to the level of 10^{11} – 10^{13} cm⁻³ had very little or no effect on the minority carrier lifetime in *p*-type silicon, or even improved it, whereas high copper concentrations inevitably led to the significant degradation of minority carrier diffusion length.⁹ In contrast, a strong effect of Cu on lifetime in *n* Si was observed even at low Cu contamination levels.^{4,10,11} A consistent explanation was offered neither for this difference in recombination activity of copper in *n* Si and *p* Si, nor for its weak impact on lifetime in *p* Si at low Cu concentrations.

In this letter, we present results of systematic experimental studies of the impact of copper contamination on minority carrier diffusion length in *n*-type and *p*-type as-grown Czochralski (CZ) silicon with different doping levels, and in *p*-type silicon with internal gettering sites, and suggest a model to explain the observed dependencies.

Copper diffusion in CZ-grown *p*-type silicon was performed in the temperature range between 450 °C and 950 °C for sufficiently long time to reach the equilibrium solubility of copper. For comparison, similar diffusions were performed using *n*-type silicon. Due to the lack of suitable CZ-

grown *n*-type samples, float-zone grown *n*-type Si samples were used. Copper was chemically deposited on the sample surfaces by dipping them into dilute copper-fluoride solution. Diffusion anneals were performed in a vertical furnace in a nitrogen ambient and were terminated by a quench in silicone oil. After the quench, samples were chemically cleaned, etched, and stored for several days at room temperature before measurements to allow all defect reactions of copper to go towards completion. The minority carrier diffusion length was determined by the surface photovoltage technique using the CMS-IIIa system by Semiconductor Diagnostics. The results of the measurements for 10 Ω cm silicon are presented in Fig. 1. We found it instructive to plot the data in Figs. 1–3 against the effective density of recombination sites, which is proportional to $1/L^2$, where L is the minority carrier diffusion length. This proportionality holds because according to the Shockley–Read–Hall statistics, the density of recombination centers is proportional to $1/\tau$ (assuming

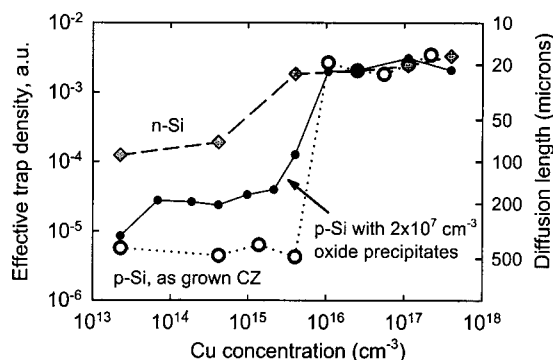


FIG. 1. Dependence of effective trap density and minority carrier diffusion length on Cu contamination level in 10 ohm cm CZ-grown *n*-Si samples (diamonds), and in 10 ohm cm *p* Si, as-grown CZ (open circles) and with 2×10^7 cm⁻³ of IG sites (black circles), as determined from optical precipitates profiler measurements.

^{a)}Electronic mail: ravinder@uclink4.berkeley.edu

^{b)}Mailing address: Lawrence Berkeley National Laboratory, MS 62-203, 1 Cyclotron Rd., Berkeley, CA 94720.

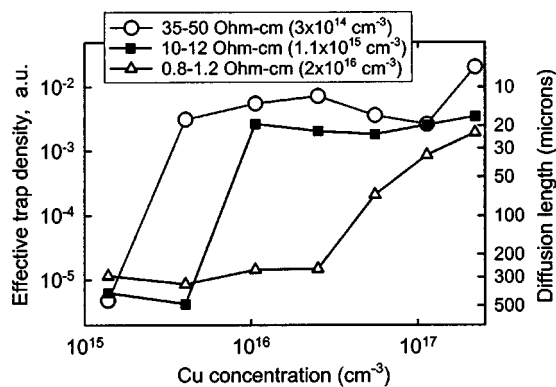


FIG. 2. Dependence of effective trap density and minority carrier diffusion length on Cu contamination level in *p*-type silicon samples with a different boron doping level.

that there is only one predominant type of lifetime limiting defects in the sample), whereas the minority carrier lifetime, τ , is proportional to L^2 . The corresponding values of the minority carrier diffusion length, L , are given in Figs. 1–3 on the right-hand side vertical axis.

Figure 1 presents three curves, one for *n*-type silicon, and two for *p*-type silicon, as-grown CZ and with internal gettering (IG) sites. The curve obtained on the sample with IG sites (filled circles) will be discussed in detail at the end of this article. Initially, our discussion will be confined to the curves obtained on the *n* Si (diamonds) and *p* Si without intentionally formed IG sites (open circles). It is seen from Fig. 1 that in *n*-type silicon, the effective density of recombination centers increases almost linearly with the indiffused Cu concentration, whereas in *p*-type silicon, the effective density of recombination centers remains very low at low Cu concentrations and experiences a sharp increase at a Cu concentration of approximately 10^{16} cm^{-3} . This critical Cu concentration matches the threshold concentration of copper that has to be reached in $10 \Omega \times \text{cm}$ *p* Si to start forming Cu precipitates in the bulk, which was reported in our recent publication.¹² The existence of a threshold Cu concentration for the formation of Cu precipitates was explained as follows.¹² Precipitation of copper in the bulk of the wafer is

unlikely at low copper concentrations because of the large nucleation barrier for the formation of Cu precipitates, which is due to (i) strong compressive strain, caused by large volume expansion¹³ during the formation of copper silicide, and (ii) electrostatic repulsion between the positively charged Cu precipitates and the ionized, interstitial Cu_i^+ ions.¹⁴ Copper precipitates were shown to be positively charged in *p* Si and negatively charged or neutral in *n* Si.⁹ The charge state of copper precipitates is determined by the Fermi level position, which depends on the concentration of shallow acceptors (boron) compensated by shallow donors (mainly interstitial copper). If the interstitial copper concentration exceeds the boron concentration, conductivity type inversion occurs. As soon as the Cu_i^+ concentration becomes sufficient for the Fermi level to exceed the electroneutrality level of the precipitates at approximately $E_C - 0.2 \text{ eV}$,⁹ the charge state of copper precipitates changes from positive to neutral or negative, and the electrostatic precipitation barrier disappears or even changes sign to attraction. In *n*-type silicon, a much lower Cu concentration is required to initiate nucleation of the precipitates since the Fermi level is close to the electroneutrality level even for very low copper concentrations.

EBIC measurements of our samples indicated that Cu precipitates are very efficient recombination centers.¹⁵ This can be explained by a combination of two factors, the positive charge of Cu precipitates in *p* Si, which increases their capture cross section for minority charge carriers, and the effective recombination of these charge carriers through the band-like states associated with Cu precipitates.^{9,14} Therefore, it is reasonable to assume that the step in minority carrier lifetime (Fig. 1) is caused by recombination of the charge carriers at copper precipitates. These precipitates are formed at high density as soon as the Fermi level position in the sample reaches the electroneutrality level, thus reducing the total barrier for nucleation and growth of Cu precipitates.

To further test this model, we investigated the effect of Cu on minority carrier diffusion length for samples with three different resistivities [$35\text{--}50 \text{ ohm cm}$ ($\langle B \rangle = 3 \times 10^{14} \text{ cm}^{-3}$), $10\text{--}12 \text{ ohm cm}$ ($\langle B \rangle = 1.1 \times 10^{15} \text{ cm}^{-3}$), and $0.8\text{--}1.2 \text{ ohm cm}$ ($\langle B \rangle = 2 \times 10^{16} \text{ cm}^{-3}$)]. This experiment enabled us to compare the minority carrier diffusion length in samples with the same starting copper concentration, but with a different Fermi level position. Results are presented in Fig. 2, which shows that the position of the step in the effective density of recombination sites depends on the doping concentration. A higher concentration of Cu is required to cause the step-like transition in the effective density of recombination sites in the samples with a higher boron doping level. However, the position of the room-temperature Fermi level calculated for the moment immediately after the quench is the same for all three types of samples, see Fig. 3. This allows us to conclude that all three samples have experienced the same dominant defect reaction, which determines the observed step in the efficient density of copper-related recombination sites: the formation of copper precipitates which starts as soon as Fermi level reaches the electroneutrality level of copper precipitates.

This result provides a confirmation of the electrostatic model of Cu precipitation in silicon^{12,14} and explains the step-like dependence of minority carrier lifetime on Cu con-

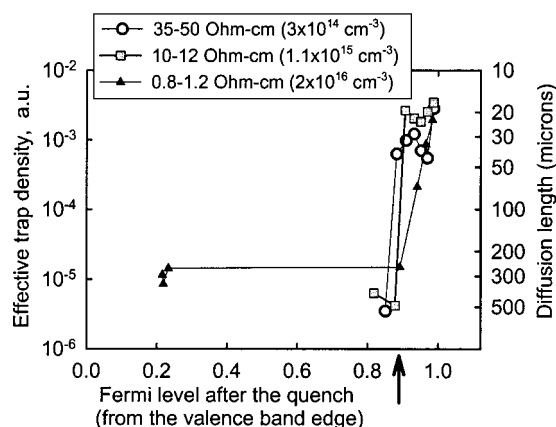


FIG. 3. The same data as in Fig. 3, plotted against Fermi level position in the sample at room temperature immediately after the quench. The Fermi level position was calculated assuming that all copper is in the ionized interstitial state. The range of the horizontal axis corresponds to the band gap width of silicon at room temperature. The arrow indicates the position of the electroneutrality level of copper precipitates.

centration in *p*-type Si. At low copper concentrations, no precipitates are formed. As discussed in our recent publications,^{16,17} complexes of interstitial copper are unstable, and outdiffusion of copper to the wafer surface is the predominant defect reaction of Cu in *p*-type silicon. Since only a small fraction of Cu is left in the bulk, its impact on minority carrier diffusion length is small, and may even result in passivation of electrically active defects, if complexes of Cu with these defects are less recombination active than the original defects. However, when the critical copper concentration is reached, copper starts forming recombination active precipitates everywhere in the bulk. As these precipitates are very efficient lifetime killers, the minority carrier diffusion length decreases drastically. In *n*-type silicon, the Fermi level is very close to the electroneutrality level of copper precipitates, and nucleation of copper precipitates occurs much easier. Therefore, the effect of copper on minority carrier lifetime at low copper concentrations is greater in *n* Si than in *p* Si.

Even with this qualitative understanding, the details of the behavior of copper and, consequently, its effect on the lifetime on the quantitative level may vary from wafer to wafer, depending on its thermal history, concentration of lattice defects and other impurities in the wafer, and its surface condition. It is instructive to compare two dependencies presented in Fig. 1, taken on boron-doped CZ samples with the same resistivity with (filled circles) and without (open circles) IG sites. The curve obtained on the sample with IG sites shows the same step-like behavior as the curve obtained on as-grown CZ sample, but the step is much smoother and its height is lower. This can tentatively be explained by heterogeneous precipitation of copper at lattice defects (e.g., dislocations or stacking faults) associated with the oxide precipitates, which results in a small increase in the effective trap density at a subcritical Cu concentration range between 10^{13} and 10^{15} cm⁻³. As the Cu concentration reaches 10^{16} cm⁻³, the effective trap density becomes approximately equal to that for as-grown CZ sample. This indicates that precipitation of Cu at oxide precipitates does not seem to be playing a significant role in determining the minority carrier diffusion length at copper concentration above the critical copper concentration.

Finally, we would like to point out that the slope of the nearly linear dependence obtained for *n*-type silicon in Fig. 1 (diamonds) suggests that the copper-related recombination centers consist of more than one atom of copper. Recombination at centers which consist of a single impurity atom should follow a proportional dependence between the metal concentration and the effective density of precipitation sites, whereby doubling of metal concentration doubles the concentration of recombination sites. In contrast, the increase in Cu concentration by over four orders of magnitude results only in an increase in efficient density of recombination sites in *n* Si by about a factor of 20 (see Fig. 1). This confirms our hypothesis that the minority carrier diffusion length is limited in *n* Si by agglomerates of copper. This is reasonable

also because it is known that interstitial copper is a very shallow donor, which, according to Shockley–Read–Hall statistics, is expected to have very weak recombination properties, and cannot account for such a strong effect (similar to that of iron) of Cu on minority carrier diffusion length in silicon.

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